

Enthalpy of Formation of Gas Hydrates

K.N. Marsh^{C, S} and G. Jun

Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

The enthalpies of formation of gas hydrates for six gas mixtures containing specified amounts of methane, ethane, propane, n-butane, iso-butane and carbon dioxide at pressures have been measured at pressures of approximately 2000 kPa and 6700 kPa. The measurements were made in a multicell differential scanning calorimeter using modified high pressure cells. The gas hydrate was formed by cycling the solution in the vicinity of the ice point. The mass of hydrate formed was calculated from the measurement of the enthalpy of fusion of water after the hydrate was formed and after the hydrate was dissociated. The enthalpy of water and the enthalpy of dissociation of the gas hydrate were determined from the calorimeter response during a slow temperature scan at constant pressure. The amount of gas released from the dissociation of hydrate was determined from the volume change of the high pressure pump required to maintain the pressure constant, and the amount of hydrate formed was determined from the measurement of the enthalpy of fusion of water before and after the dissociation of hydrate. The occupation number (the ratio of the water to gas) and the enthalpy of hydrate formation have an uncertainty of 1.5 %. The results show that the enthalpies of hydrate formation and the occupation number are essentially independent of pressure. In addition, the temperatures of dissociation of the hydrates agree well with literature values.